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## Siewert et al.

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		86413	7/1975	Ja
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420/46; 148/327, 440

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	148/442; 148/327
F501	Field of Search 420/58/1 1/5

## [56] **I**

#### References Cited

## U.S. PATENT DOCUMENTS

2,156,298	3/1937	Leitner.
2,256,614	6/1940	Franks .
2,398,702	2/1941	Fleischmann .
2,671,726	11/1950	Jennings .
2,696,433	12/1954	Tanczyn .
2,839,391	6/1958	Loveless .
3,337,331	8/1967	Ljungberg .
3,384,476	11/1967	Egnell.
3,859,083	1/1975	Kusaka et al
4,012,227	3/1977	Forbes Jones et al
4,014,680	3/1977	Reen .
4,141,762	2/1979	Yamaguchi et al
4,248,629	2/1981	Pons et al
4,285,787	8/1981	Garner et al
4,302,247	11/1981	Abe et al
4,324,584	4/1982	Marizy .
4,400,349	8/1983	Kudo et al 420/584.1
4,560,408	12/1985	Wilhelmsson .
4,997,040	3/1991	Cizek .
5,021,215	6/1991	Sawargi et al

#### FOREIGN PATENT DOCUMENTS

449702	7/1948	Canada .
528102	7/1956	Canada.
7107	7/1962	Japan .
86415	7/1975	Japan .

86414	7/1975	Japan .
86413	7/1975	Japan .
86412	7/1975	Japan .
16153	1/1982	Japan .
617194	2/1949	United Kingdom .
657021	9/1951	United Kingdom .

#### OTHER PUBLICATIONS

McCowan, C. N., and Siewert, T. A., Advances in Cryogenic Engineering-Materials, vol. 34 (Plenum Press 1988), pp. 335-342.

Morris, J. W., Advances in Cryogenic Engineering-Materials, vol. 32 (Plenum Press 1986), pp. 1–22.

Reed, R. P., Purtscher, P. T., and Yushcbenko, K. A., Advances in Cryogenic Engineering–Materials, vol. 32 (Plenum Press 1986), pp. 43–50.

(List continued on next page.)

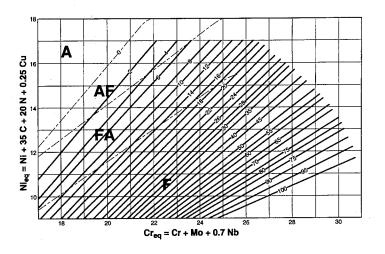
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### [57] ABSTRACT

An alloy comprising nickel, chromium, molybdenum, manganese, nitrogen and iron in amounts such that a weld metal formed therefrom is austenitic, wherein nitrogen is present in a concentration of from about 0.1 to about 0.2% of the alloy in weight percent. The weld metals prepared from the alloys of the present invention possess superior properties as compared to other stainless steels. These properties include inter alia a superior tearing modulus, fracture toughness, and yield strength, even at cryogenic temperatures.

The present invention further provides a method for welding a metal part which is intended for exposure to cryogenic temperatures comprising welding the metal part using a welding electrode comprising nickel, chromium, molybdenum, manganese, nitrogen and iron in amounts such that a weld metal formed therefrom is austenitic, wherein nitrogen is present in the electrode in a concentration of from about 0.1 to about 0.2% of the electrode in weight percent. Preferably, the welding comprises gas metal arc welding, wherein shielding gas used during welding contains no more than about 2% oxygen by volume.

#### 12 Claims, 5 Drawing Sheets



#### OTHER PUBLICATIONS

McCowan, C. N., and Siewert, T. A., Advances in Cryogenic Engineering-Materials, vol. 36, (Plenum Press 1990), pp. 1331–1338.

Simon, N. J., and Reed, R. P., J. Nucl. Mater., vol. 141–43 (1986), pp. 44–48.

Siewert et al., Welding Metallurgy of Structural Steels. Proc. Int. TMSEWI Symposium, Denver, (Feb. 22–26, 1987), pp. 415–425.

McCowan, C. N., Siewert, T. A., and Tobler, R. L., J. Eng. Mater. & Technol., vol. 108 (Oct. 1986), pp. 340-43.

Yamagami N., Kohsaka, Y., and Ouchi, C., Advances in Cryogenic Engineering-Materials, vol. 34 (1988), pp. 359-66.

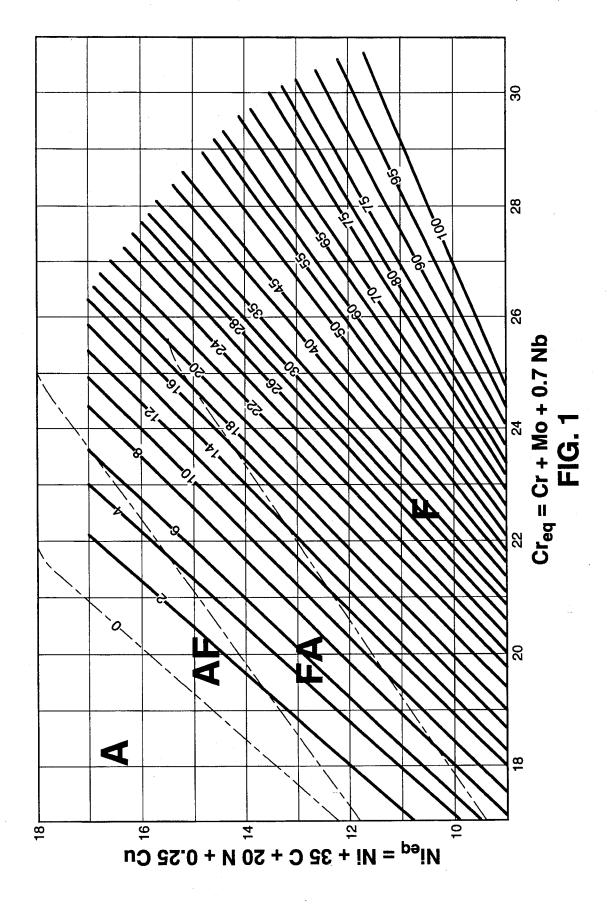
Kim, J., Oh, B., Youn, J., Gan-Woong, B., and Hae-Moo L, Advances in Cryogenic Engineering-Materials, vol. 36 (1990), pp. 1339-46.

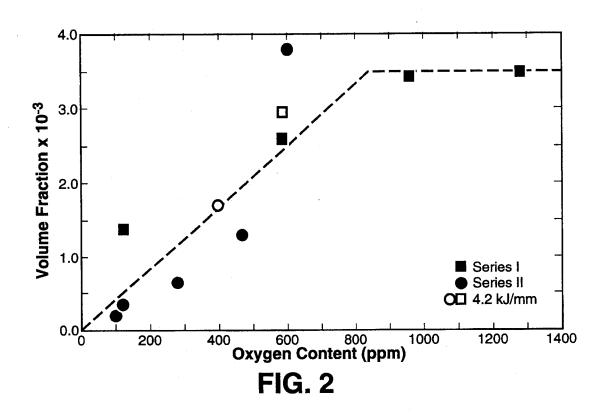
Gladman, T., Dulieu, D., and Melvor, I. D., Structure–Property Relationships in High–Strength Microalloyed Steels, Microalloying 75 (1975), pp. 32–55. Hahn, G. T., and Rosenfield, A. R., Metall, Trans., vol. 6A (1975), pp. 653–68.

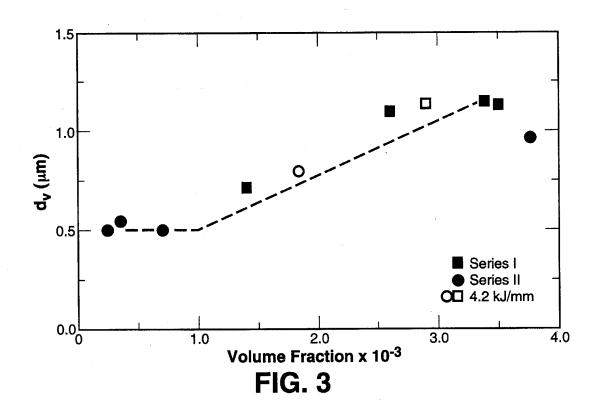
Garret, G. G., and Knott, J. F., Metall. Trans. vol. 9A (1978), pp. 1187–201.

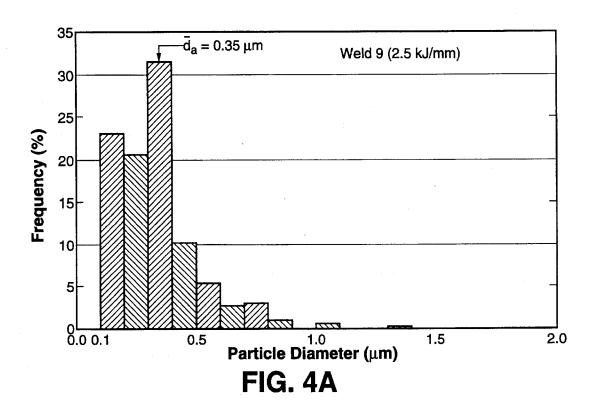
Schwalbe, K. H., Eng. Fract. Mech., vol. 9 (1977), pp. 795-847.

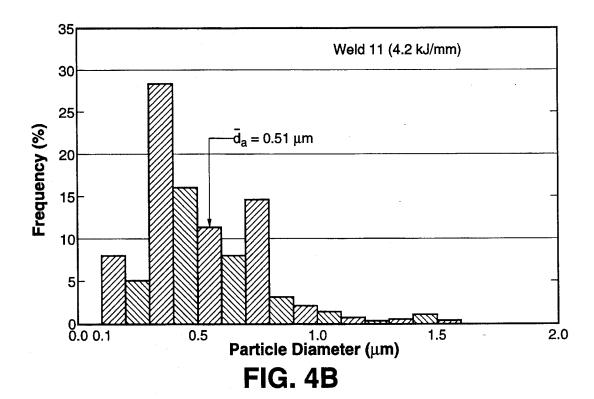
LeRoy, G., Embury, J. D., Edwards, G., and Ashby, M. F., Acta metall., vol. 29 (1981), pp. 1509–1520.

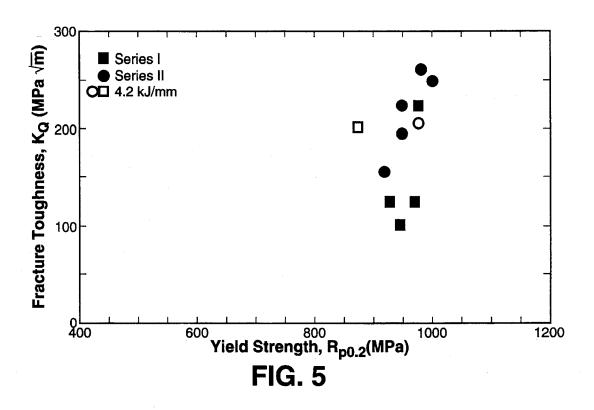


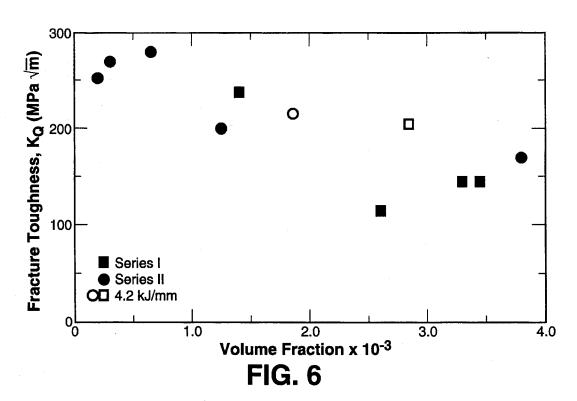


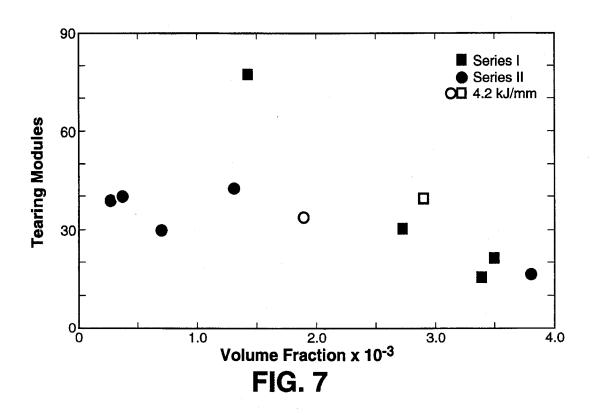


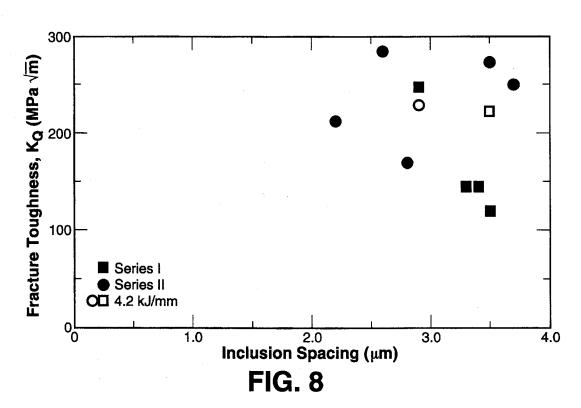












1

#### ALLOYS FOR CRYOGENIC SERVICE

#### FIELD OF THE INVENTION

The present invention relates generally to metal alloys More specifically, the invention relates to alloys that are useful as welding electrodes and, more particularly, electrodes which are able to form weld metals which are able to withstand exposure to cryogenic temperatures.

#### BACKGROUND OF THE INVENTION

Over the last few years, research into superconducting magnets has progressed to the level where application of this technology is becoming a practical reality. As superconducting magnets typically must operate at cryogenic temperatures, e.g., down to about 77 K. and as low as 4 K., enclosures and devices used in the various applications of such magnets must necessarily also be able to withstand those extreme temperatures without failing. One example of such a material that has been used to prepare enclosures for one such application, e.g., coil cases for superconducting magnets, is stainless steel.

In the past, stainless steel alloys were formulated and developed so as to maximize their performance at high temperatures. This was primarily due to such alloys' known superior resistance to oxidation at those high temperatures as well as a lack of knowledge as to any applications for such alloys at cryogenic temperatures, e.g., superconducting magnet applications. Examples of such stainless steel alloys which are said to provide the aforesaid high temperature performance include those described in U.S. Pat. Nos. 2,696,433 and 2,839,391.

With the increasing interest in superconducting magnet applications, the evaluation of the properties of various stainless steel alloys at cryogenic temperatures has been undertaken with greater frequency. During such evaluations, it was found that at cryogenic temperatures, weld metals formed from stainless steel electrodes typically possessed a toughness which is significantly lower than that of the corresponding base metal alloy. Therefore, during the past fifteen years, certain studies have been undertaken in an effort to focus upon improving the physical properties of stainless steel welding metals, prepared from welding electrodes, in general at cryogenic temperatures.

One such study evaluated three welding electrodes (which will also be referred to herein as alloys) after they had been formed into a weld metal. This study determined that a ferrite-free 18Cr-16Ni-9Mn-0.14N electrode, when formed into a weld metal, exhibited the best combination of toughness (20 ft-lb Charpy V-notch (CVN) absorbed energy) and strength (124 KSI, 0.2% yield) at 77 K. The particular electrode which resulted in the preparation of a weld metal possessing the highest degree of toughness (28 ft-lb CVN) had a composition which can be generally described as 14Cr-20Ni-9Mn-0.08N (91 KSI, 0.2% yield) at 77 K. Fickett et al., Materials Studies for Magnetic Fusion Energy Applications at Low Temperatures— I, NBSIR 78-884 (April, 1978), pp. 173 & 174.

A second study evaluated three alloys and determined that the electrode from which a weld metal having the highest CVN (46 ft-lb) at 77 K. was prepared was an alloy comprised of 18Cr-16Ni-9Mn-0.08N (135 KSI, 2% yield strength). The yield strengths of three additional weld metals 65 were evaluated at 4 K., with an alloy comprising 18Cr-14Ni-2Mo-0.07N providing a weld metal having the greatest

2

strength (132 KSI) at 4 K., while exhibiting a toughness of 52 ft-lb CVN (after annealing) at 77 K. Fickett et al., Materials Studies for Magnetic Fusion Energy Applications at Low Temperatures—II, NBSIR 79-1609 (June 1979).

5 Despite these advances however, neither of these studies offer any indication as to how the toughness and strength of weld metals prepared from stainless steel alloys could be improved, particularly if a weld metal prepared from such alloys was intended to be exposed to temperatures as low as 10 4 K.

Thus, and despite the availability of the aforesaid known alloys from which weld metals can be prepared, there remains a need for an alloy which, when formed into an electrode, enables one to prepare a welded stainless steel structure, wherein the weld metal formed from the electrode possesses a strength and toughness superior to that of existing weld metals, even when exposed to cryogenic temperatures, e.g., 77 K. and as low as 4 K.

The present invention provides such an improved alloy. These and other advantages of the present invention, as well as additional inventive features, will be apparent from the description of the invention provided herein.

#### SUMMARY OF THE INVENTION

The present invention provides an austenitic alloy comprising nickel, chromium, molybdenum, manganese, nitrogen and iron in amounts such that a weld metal formed therefrom is austenitic, wherein nitrogen is present in the alloy in a concentration of from about 0.1% to about 0.2% of the alloy in weight percent.

Most preferably, the austenitic alloy comprises nickel at a concentration of about 25%, chromium at a concentration of about 21%, molybdenum at a concentration of about 5%, manganese at a concentration of about 7%, copper at a concentration of about 1.6%, nitrogen at a concentration of about 0.19%, phosphorus and sulfur which, in combination, are present in the alloy at a concentration of less than about 0.015%, oxygen at a concentration of less than about 0.015%, and the balance iron, all in weight percentages.

The weld metal prepared using the alloy of the present invention possesses superior properties, upon exposure to cryogenic temperatures, as compared to known stainless steel alloys. These properties of the weld metal include inter alia a superior tearing modulus, fracture toughness, and yield strength.

The present invention further provides a method which comprises welding a metal part, which part is intended for exposure to cryogenic temperatures, comprising welding the metal part using a welding electrode which provides an austenitic weld metal, the electrode comprising nickel, chromium, molybdenum, manganese, nitrogen and iron in amounts such that a weld metal formed therefrom is austenitic, wherein nitrogen is present in a concentration of from about 0.1 to about 0.2% of the alloy in weight percent. Preferably, the welding comprises gas metal arc welding, wherein the shielding gas used during the welding contains no more than about 2% oxygen by volume.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a constitution diagram for stainless steel alloys and weld metals used for determining the ferrite content of such metals.

FIG. 2 is a plotted graph which demonstrates the relationship between inclusion volume fraction and weld metal oxygen content.

3

FIG. 3 is a plotted graph which demonstrates the relationship between mean three-dimensional (3-D) particle diameter and inclusion volume fraction.

FIG. 4(a) illustrates the effect of heat input on the two-dimensional (2-D) inclusion size distribution for weld  $^5$  no. 9.

FIG. 4(b) illustrates the effect of heat input on the two-dimensional (2-D) inclusion size distribution for weld no. 11.

FIG. 5 illustrates the effect of yield strength on weld metal fracture toughness.

FIG. 6 illustrates the effect of inclusion volume fraction on weld metal fracture toughness.

FIG. 7 illustrates the effect of inclusion volume fraction 15 on weld metal tearing modulus.

FIG. 8 illustrates the effect of mean center-to-center inclusion volume spacing on weld metal fracture toughness.

# DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention may best be understood with reference to the accompanying drawings and in the following detailed description of the preferred embodiment.

The present invention provides a novel stainless steel alloy which, when configured into a welding electrode and welded so as to form a weld metal, provides a weld metal having advantageous properties in the areas of strength and toughness even when exposed to cryogenic temperatures. This alloy is a stainless steel which comprises nickel, chromium, molybdenum, manganese, nitrogen and iron in amounts such that a weld metal formed therefrom is austenitic, wherein nitrogen is present in a concentration of from about 0.1% to about 0.2% of the alloy in weight percent. For purposes of describing the present invention, and unless otherwise noted, all percentages should be construed as referring to weight percentages.

As mentioned above, the stainless steel weld metals of the present invention are austenitic in nature, i.e., no other phase structures are present therein. The existence of such phases in a weld metal, or alloy if desired, e.g., an electrode, can be readily determined by reference to FIG. 1. The weld metal of the present invention falls within the austenitic only section of that figure, that section being denoted by the letter "A". A description of the proper use of that figure is described in Kotecki et al., Welding Research Supplement, (May, 1992), pp. 171-s to 78-s.

One of the objects of the present invention is to provide an alloy which, when formed into a weld metal during a welding procedure, provides a weld metal which possesses a relatively high level of strength and toughness at cryogenic temperatures. In pursuing this objective, it was found that by including nickel in the alloy in certain amounts that an increase in weld metal toughness at cryogenic temperatures was experienced. In order to achieve the aforesaid performance, it was discovered that nickel should advantageously be present in the alloy at a concentration of at least about 12% of the alloy, advantageously from about 12% to about 50%, preferably from about 20% to 30%, and most preferably about 25%.

It was further discovered that, when the oxygen content of the weld metal was controlled below a certain limit, a weld metal having superior toughness resulted. The oxygen in the 65 weld metal is present in the form of oxide inclusions, which are the nucleation sites for the fracture of the weld metal. As 1

the number of inclusions is reduced by reducing the oxygen content (assuming the size distribution remains approximately constant), these inclusions become further apart, requiring the nucleation cracks to travel a greater distance before joining, thus providing a weld metal with a high degree of toughness. In particular, the oxygen content of the weld metal in accordance with the present invention is advantageously less than about 0.06% (600 parts per million) in the weld metal (including the oxygen present in the electrode, e.g., preferably about 0.01% and any oxygen provided by the shielding gas used during welding, e.g., about 0.05%). Preferably, the oxygen content in the weld metal will be less than about 0.03%. Lower percentages of oxygen are preferably used to provide weld metals having greater toughness. To achieve such oxygen levels in the weld metal, the oxygen content in the electrode used to form the weld metal is advantageously kept below about 0.03%, and preferably below about 0.01%.

Many prior art alloys designed to provide a weld metal having an austenitic phase will typically further include at least a small amount of a ferrite phase for the purpose of controlling cracking sensitivity during solidification. Ferrite is measured in units of FN, which is approximately equal to volume percent at small numbers. In contrast to the aforementioned weld metals, the weld metal and alloy of the present invention should contain no ferrite as ferrite has lower toughness than austenite at cryogenic temperatures.

In order to provide adequate cracking resistance during solidification in the weld metal of the present invention, it was discovered that such resistance could be controlled within acceptable limits by carefully controlling the phosphorus and sulfur content of the weld metal. In particular, the total phosphorus and sulfur content of the alloy from which the weld metal is prepared, in combination, should be advantageously limited to less than about 0.015% of the alloy. When this is accomplished, the resulting weld metal will also meet the aforesaid limits of sulfur and phosphorus content.

It was further discovered that when one included manganese in the alloy at a concentration of at least about 3% of the alloy, one would advantageously experience greater nitrogen solubility in the weld pool, higher strength in the resulting weld metal, and desulfurization of the weld pool. In view of this, manganese is advantageously present in the alloy from about 3% to about 15%, preferably from about 5% to about 10%, and most preferably about 7%.

In addition to the components identified previously, copper is a further component which may be included in the alloy of the present invention. Specifically, it was discovered that the combination of molybdenum and copper will increase the strength and will have a positive impact upon the cracking resistance of the weld metal during solidification. Preferably then, molybdenum is present in the alloy at a concentration of about 3% to about 10%, and copper is present in the alloy at a concentration of about 1% to about 2%. Most preferably, those two components are present in concentrations of about 5% and about 1.6%, respectively.

Advantageously then, the alloy of the present invention should include nickel at a concentration ranging from about 12% to about 50%, manganese in an amount greater than about 3%, and the remaining alloy components in concentrations such that the weld metal prepared therefrom possesses a tearing modulus of less than about 50, a fracture toughness of at least about 150 MPa/m, and a yield strength of at least about 900 MPa at 4 K.

In order to achieve the aforesaid performance level at

5

cryogenic temperatures, the alloy of the present invention advantageously comprises nickel at a concentration of from about 12% to about 50%, chromium at a concentration of from about 12% to about 30%, molybdenum at a concentration of from about 3% to about 10%, manganese at a concentration of from about 3% to about 15%, and nitrogen at a concentration of about 0.1% to about 0.3%.

Preferably, the alloy of the present invention comprises nickel at a concentration ranging from about 20% to about 30%, chromium at a concentration of about 15% to about 25%, molybdenum at a concentration of about 3% to about 8%, manganese at a concentration of about 5% to about 10%, copper at a concentration of about 1% to about 2%, and nitrogen at a concentration of about 0.15% to about 0.25%.

Most preferably, the alloy of the present invention comprises nickel at a concentration of about 25%, chromium at a concentration of about 21%, molybdenum at a concentration of about 5%, manganese at a concentration of about 7%, copper at a concentration of about 1.6%, nitrogen at a concentration of about 0.19%, and phosphorus and sulfur which, in combination, are limited to less than about 0.015% of the alloy.

As methods of preparing the alloys of the present invention are well known to those of ordinary skill in the art, such methods are not described herein. However, as it has been discovered that the method of welding will effect the resulting weld metal oxygen and nitrogen content, such will be discussed herein.

The present invention further provides a method for using 30 the alloys of the present invention. Advantageously, there is provided a method for welding a metal part wherein the welded part is intended for exposure to cryogenic temperatures. The method comprises welding a metal part using a welding electrode which provides a weld metal, wherein the 35 electrode comprises an alloy of the present invention, as described previously. Preferably, the welding comprises gas metal arc welding, wherein the shielding gas contains no more than about 2% oxygen by volume. Such low levels of oxygen have been found to provide further increases in the 40 fracture toughness of the weld metal. This is due to the discovery that the inclusion volume fraction of the weld metal was lowered, increasing at least its toughness, when the oxygen level in the weld metal was lowered. Thus, in the case of the weld metal, the amount of oxygen used in the 45 shielding gas should be limited such that the oxygen content in the resulting weld metal is less than about 0.06% and preferably less than about 0.04%.

In addition to oxygen, nitrogen may also be added to the weld pool during welding through its presence in the shielding gas. The amount of nitrogen in the alloy, as well as weld metal however should be controlled within certain limits. Although higher levels of toughness are experienced with higher levels of nitrogen in the weld metal, such must be balanced against the introduction of unwanted porosity in the weld metal which results at higher nitrogen levels. Porosity in the weld metal is a property that results from nitrogen's relatively higher solubility in liquid metals, e.g., when the electrode is liquid during welding (the weld pool),

6

as opposed to its solubility when the weld metal solidifies. Specifically, if there is an excess of nitrogen in the weld pool, as the weld pool solidifies and forms the weld metal, the nitrogen, because of its lower solubility in solidified metal, will form air bubbles in the metal. Such air bubbles introduce defects into the weld metal, thereby decreasing its physical and mechanical properties. Therefore, the aforementioned controls must be placed upon the amount of nitrogen in the alloy and weld metal in order to maximize the physical and mechanical properties of the weld metal.

The following example further illustrates the present invention but, of course, should not be construed as in any way limiting its scope.

#### **EXAMPLE**

Two 1.2 mm diameter, gas metal arc electrode welding rods were prepared using conventional processing known to those of skill in the art. The composition of those rods, which were fully austenitic in nature, is provided in Table 1.

TABLE 1

Element	Wire No. 1	Wire No. 2
Cr	19.40	21.36
Ni	24.24	25.16
Mo	4.17	5.16
Mn	1.76	7.22
N	0.056	0.190
С	0.01	0.01
Si	0.29	0.39
P	0.008	0.005
S	0.001	0.002
Co	0.045	_
Cu	1.46	1.61

The most preferred alloy of the present invention, which can be used to prepare a weld metal, is a variation of a commercial composition known as 904L when in base plate form and as 385 when in electrode form. Such are available from various sources, including Sandvik of Scranton, Pa. Such commercial compositions are represented by wire no. 1 as described in Table 1.

Two weld series were prepared, using wire no. 1 for Series I and wire no. 2 for Series II. Within each series, systematic variations in the weld metal oxygen content (which can also be expressed as inclusion volume fraction) were achieved by varying the oxygen content of the shielding gas. For those welds, the heat input was kept fairly constant at 2.5 kJ/mm in order to obtain a relatively equal inclusion size distribution. To obtain differences in the inclusion size distribution at a given volume fraction, one weld within each series was deposited at a higher heat input of 4.2 kJ/mm.

All welds were deposited to single V-grooves on type base plates, 25 mm thick, and the groove geometry was as specified in American Welding Society Standard A 5.5-81 (AWS, Miami, Fla. (1981)). The electrode extension was 19 mm and the interpass temperatures were 150° C. Table 2 contains operational conditions for the two weld series.

TABLE 2

Series	Weld	Current (A)	Voltage (V)	Travel Speed (mm/s)	Heat Input (kJ/mm)	Shield Gas (16.5 l/m)
I	1	210	31	2.8	2.5	Ar + 5% N <sub>2</sub>
	2	245	31	3.0	2.5	$Ar + 5\% N_2 + 2\% O_2$
	3	255	29	3.0	2.5	$Ar + 5\% N_2 + 5\% O_2$
	4	250	29	2.9	2.9	Ar + 5% $N_2 + 10\% \tilde{O}_2$
	5	320	33	2.5	4.2	$Ar + 5\% N_2 + 2\% O_2$
II	6	270	31	3.4	2.5	$Ar + Ar/10\% N_2$
	7	280	31	3.5	2.5	Ar
	8	280	30	3.4	2.5	Ar + 0.5% O <sub>2</sub>
	9	270	31	3.4	2.5	$Ar + 2\% O_2$
	10	290	28	3.3	2.5	$Ar + 5\% O_2$
	11	390	32	3.0	4.2	$Ar + 2\% O_2$

Weld no. 6 utilized a dual-gas-shield configuration as described in McCowan et al., *Advances in Cryogenic Engineering-Materials*, 36 (Plenum Press 1990), p. 1331.

After the welds were completed, for each weld, one all weld metal uniaxial tensile specimen (6.25 mm diameter, 25.4 mm gauge length) and two through-thickness compact tension specimens (CTS) were machined for testing in liquid helium (4 K). The CTS were tested in accordance with 25 ASTM Standard E 813-89, using the single-specimen compliance method, while the tensile specimens were strained at a constant cross-head speed of 0.5 mm/min.

For metallographic testing purposes, they were sectioned transverse to the welding direction and subsequently prepared using standard grinding and polishing techniques for metallographic examination. The two-dimensional (2-D) inclusion volume fraction and size distribution were determined by scanning electron microscopy in combination with an automatic image analysis at a magnification of 2500×, 35 using ordinary polished specimens. A total of 500 particles

The weld metal oxygen and nitrogen contents are given in Table 3, in weight percentages.

TABLE 3

Weld No.	Oxygen	Nitrogen
1	0.0102	0.165
2	0.0567	0.158
3	0.1274	0.140
4	0.0928	0.115
5	0.0568	0.128
6	0.0095	0.150
7	0.0121	0.149
8	0.0231	0.158
9	0.0463	0.134
10	0.0589	0.144
11	0.0379	0.147

Measured values for the inclusion volume fraction are provided in Table 4. The inclusion volume fractions reflect the differences in the oxygen content of the weld metal.

TABLE 4

.0 <sup>3</sup> π <sup>2</sup> ) λ <sub>ν</sub> (μm)
2.9
3.5
3.3
3.4
3.5
3.7
3.5
2.6
2.2
2.8
0 6 1 9

Note: The abbreviations used in Table 4 are as follows: Inclusion volume fraction  $(V_{\nu})$ , arithmetic means two-dimensional particle diameter  $(d_a)$ , arithmetic means three-dimensional particle diameter  $(d_{\nu})$ , number of particles per unit volume  $(N_{\nu})$ , number of particles per unit area  $(N_a)$ , and mean particle center-to-center volume spacing  $(\lambda_{\nu})$ .

were counted in each instance. In these measurements, due care was taken to ensure that all particles present immediately beneath the metal surface were discriminated through proper adjustment of the microscope operating parameters. Kluken et al., *Material Science Technology*, 4 (1988), p. 648. Following inclusion analysis, the samples were etched with a mix acid (15 ml HCl, 15 ml lactic acid, and 3 ml HNO<sub>3</sub>) and the average grain size was determined in a light microscope by means of the mean linear intercept technique. ASTM Standard No. E112-84 (1984). In addition, a selected 65 number of broken CTS's were examined to reveal the fracture mode.

A plot of the inclusion volume fraction versus the weld metal oxygen content is shown in FIG. 2. Within the considerably scattered data, the inclusion volume fraction appears to be proportional to the oxygen content up to approximately 0.08 wt. % oxygen. Above that level the inclusion volume fraction is seen to be independent of the oxygen content.

The arithmetic mean three-dimensional (3-D) particle diameters, dv, provided in Table 4, were calculated from the measured two-dimensional (2-D) particle diameters,  $d_a$ , using the Fullman equation:

$$d_{\nu} = \frac{\pi}{2} d_a.$$

See Fullman, AIME, 197 (1953), p. 447.

The plot in FIG. 3 shows that the arithmetic mean 3-D inclusion diameter is independent of the inclusion volume fraction up to a value of about  $1\times10^{-3}$ . A further increase in the volume fraction is accompanied by a coarsening of the inclusions.

Examples of measured inclusion histograms are presented in FIGS. 4(a) and 4(b). As shown by the two plots, size distribution of the inclusion is strongly affected by an increase in the heat input. At 2.5 kJ/mm, the arithmetic mean 2-D inclusion diameter is equal to 0.35 µm while an increase in the heat input to 4.2 kJ/mm gives rise to a 45% increase in the mean particle diameter, to 0.51 µm.

istry of a selected number of particles. The results from those analyses revealed a shift in the inclusion chemical composition from spherical manganese silicates to predominantly angular chromium oxides with increasing weld-metal oxygen content. This was particularly true for welds within Series I. The observed shift in the chemical composition of inclusions is most likely due to the low manganese content of the filler wire used in this series.

The results of the tensile testing are summarized in Table 5. The data reveal an offset yield strength,  $R_{p0.2}$ , within a range of 870 MPa to 995 MPa, and an ultimate tensile strength,  $R_{w}$ , ranging from 1075 MPa to 1337 MPa. In addition, a minimum value of 21% has been obtained for elongation at fracture and 17% for reduction of area. An exception to this is weld 3. However, the low values experienced for this weld were due to a weld defect.

TABLE 5

Series	Weld	Yield Strength R <sub>p0.2</sub> (MPa)	Tensile Strength R <sub>m</sub> (MPa)	Elongation at Fracture (%)	Reduct. of Area (%)	Fracture Tough. K <sub>Q</sub> (MPa\m)	Tearing Modulus
I	1	969	1236	21	27	251	79
	2	938	1310	30	24	116	19
	3	970	1075	7	6	139	21
	4	921	1250	34	28	139	15
	5	870	1159	29	17	224	40
II	6	937	1301	49	39	250	39
	7	995	1337	49	42	272	40
	8	973	1222	26	24	286	29
	9	940	1271	39	27	218	44
	10	912	1275	42	39	170	16
	11	964	1283	39	30	231	33

Considering the austenite grain size, an increase in the heat input had no significant effect. For all welds in the present example, the grain size was found to be about 500 cm

Since most of the inclusions were found to be either 40 spherical or angular in shape, important inclusion characteristics such as (a) the number of particles per unit volume,  $N_{\nu}$ , (b) the number of particles per unit area,  $N_{\alpha}$ , and (c) the mean particle spacing,  $\lambda_{\nu}$ , can be calculated from the basic stereometric relationships:

$$N_{\nu} = \frac{6V_{\nu}}{\pi (d_{\nu})^3} ,$$

 $N_a=N_{\nu}d_{\nu}$ 

and

 $\lambda_{\nu}=0.554(1/N_{\nu})^{1/3}$ .

See Ashby et al., *TMS-AIME*, 236 (1966), p. 1396; Underwood, *Quantitative Stereology*, (Addison-Wesley, London, 1970), p. 109.

Calculated values for  $N_{\nu}$ ,  $N_{a}$ , and  $\lambda_{\nu}$ , are presented in 60 Table 4. A closer inspection of these data reveals that the inclusion density varies from  $3.4\times10^6$  to  $15.38\times10^6$  particles/mm<sup>3</sup> which is equivalent to a mean center-to-center inclusion volume spacing of 3.7 to 2.2  $\mu$ m.

Although no attempts were made to fully characterize the 65 non-metallic inclusions regarding chemical composition, qualitative microanalysis was used to determine the chem-

The results of J-testing are also provided in Table 5.

The yield strength, tensile strength, elongation as fracture, and reduction of area were all determined using ASTM Standard E-8. Fracture toughness was determined using ASTM Standard E-813. Crack-growth fracture toughness is evaluated by a dimensionless tearing modulus (T) where:

$$T = \frac{E}{\sigma_{y}^{2}} \frac{dJ}{d(\Delta a)}$$

wherein  $dJ/d(\Delta a)$  is the average slope of the stable crack extension portion of the J vs.  $\Delta a$  plot constructed in accordance with ASTM Standard E 813. See Ashby, p. 1396.

For Series I, the fracture toughness falls within a range of 116 MPa√ m to 251 MPa√ m with a dimensionless tearing modulus ranging from 19 to 79. The welds within Series II, on the other hand, exhibited a higher fracture toughness, ranging from 170 MPa√ m to 286 MPa√ m, and a tearing modulus within a range of 16 to 44.

Without desiring to be bound to any particular theory, the lower fracture toughness of the welds within Series I may be attributed to the observed shift in the inclusion morphology with increasing weld metal oxygen content. Angular inclusions give rise to higher stress concentration than spherical inclusions.

FIG. 5 is a plot of the fracture toughness versus the weld metal yield strength. As evidenced by the plot, the observed range in yield strength is not responsible for the recorded variations in the fracture toughness.

Plots of the fracture toughness and the tearing modulus versus the inclusion volume fraction are provided in FIGS. 6 and 7, respectively. Although there is some scatter in the

data, the energy required for crack initiation and crack propagation are seen to decrease as the inclusion volume fraction increases. Also, the high heat input welds exhibit somewhat better fracture properties compared to their low heat input counterparts. As Table 4 demonstrates, the mean 5 particle center-to-center volume spacing on the former welds is slightly larger that the latter, and this may explain the better fracture properties. However, the plot shown in FIG. 8 suggests that the inclusion spacing is not a good overall fracture parameter under the prevailing circum- 10 stances.

The fractographic examinations indicated that all the welds failed in a ductile manner, with fracture surfaces exhibiting typical ductile dimple morphologies. It was also evident from those fractographs that the dimple size 15 increased with increasing particle diameter.

All of the references cited herein, including publications, standards, patents, and the like, are hereby incorporated in their entireties by reference.

While this invention has been described with an emphasis 20 upon a preferred embodiment, it will be obvious to those of ordinary skill in the art that variations of the preferred products and methods may be used and that it is intended that the invention may be practiced otherwise than as specifically described herein. Accordingly, this invention 25 includes all modifications encompassed within the spirit and scope of the invention as defined by the following claims.

What is claimed is:

- 1. An alloy comprising nickel at a concentration ranging from about 12% to about 20%, manganese at a concentration 30 ranging from about 3% to about 7%, nitrogen at a concentration ranging from about 0.15% to about 0.2%, chromium at a concentration ranging from about 15% to about 25%, molybdenum at a concentration ranging from about 3% to about 10%, copper, and the balance being iron, wherein 35 nickel, nitrogen, chromium, and molybdenum are present in effective amounts such that the alloy is austenitic, all in weight percentages of the alloy.
- 2. The alloy according to claim 1, further comprising phosphorous and sulfur, wherein phosphorous and sulfur in 40 combination are present in a concentration of less than about 0.015% of the alloy in weight percent.
- 3. The alloy according to claim 1, wherein nickel is present in the alloy at a concentration of about 20%, chromium is present in the alloy at a concentration of about 45 21%, molybdenum is present in the alloy at a concentration of about 5%, manganese is present in the alloy at a concentration of about 7%, copper is present in the alloy at a concentration of about 1.6%, and nitrogen is present in the alloy at a concentration of about 0.19%, all in weight 50 percentages of the alloy.
- 4. An alloy comprising chromium at a concentration ranging from about 12% to 19.4%, molybdenum at a concentration of 3%, nitrogen at a concentration ranging from about 0.15% to about 0.2%, nickel at a concentration rang-

ing from about 20% to about 30%, manganese at a concentration ranging from about 5% to about 10%, copper, and the balance being iron, wherein nickel, nitrogen, chromium, and molybdenum are present in effective amounts such that the alloy is austenitic, all in weight percentages of the alloy.

- 5. A weld metal obtained by welding an alloy comprising nickel at a concentration ranging from about 12% to about 20%, manganese at a concentration ranging from about 3% to about 7%, nitrogen at a concentration ranging from about 0.15% to about 0.2%, chromium at a concentration ranging from about 15% to about 25%, molybdenum at a concentration ranging from about 3% to about 8%, copper, and the balance being iron, wherein nickel, nitrogen, chromium, and molybdenum are present in effective amounts such that the alloy is austenitic, all in weight percentages of the alloy.
- 6. The weld metal according to claim 5, wherein nickel is present in the alloy at a concentration of about 20%, chromium is present in the alloy at a concentration of about 21%, molybdenum is present in the alloy at a concentration of about 5%, manganese is present in the alloy at a concentration of about 7%, copper is present in the alloy at a concentration of about 1.6%, and nitrogen is present in the alloy at a concentration of about 0.19%, all in weight percentages of the alloy.
- 7. A weld metal obtained by welding an alloy comprising chromium at a concentration ranging from about 12% to 19.4%, molybdenum at a concentration of 3%, nitrogen at a concentration ranging from about 0.15% to about 0.2%, nickel at a concentration ranging from about 20% to about 30%, manganese at a concentration ranging from about 5% to about 10%, copper, and the balance being iron, wherein nickel, nitrogen, chromium, and molybdenum are present in effective amounts such that the alloy is austenitic, all in weight percentages of the alloy.
- 8. The weld metal according to claim 7, wherein nickel is present in the alloy at a concentration of about 25%, manganese is present in the alloy at a concentration of about 7%, copper is present in the alloy at a concentration of about 16%, and nitrogen is present in the alloy at a concentration of about 0.19%, all in weight percentages of the alloy.
- 9. The alloy according to claim 1 further comprising oxygen, wherein the oxygen content of the alloy does not exceed about 0.03%, in weight percentage of the alloy.
- 10. The weld metal according to claim 5 further comprising oxygen, wherein the oxygen content of the alloy does not exceed about 0.03%, in weight percentage of the alloy.
- 11. The weld metal according to claim 10, wherein the oxygen content of the alloy does not exceed about 0.03 weight percent of the alloy.
- 12. The alloy according to claim 9, wherein the oxygen content does not exceed about 0.01 weight percent of the alloy.

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